

Geochemistry

Notes VII: Thermodynamics (1)

I. Basic concepts

II. Heat

III. Work

IV. Internal Energy and 1st Law

V. Enthalpy

VI. Entropy and 2nd and 3rd Laws

VII. Gibbs Free Energy

VIII. Equilibrium constants

IX. Activity

X. P, T, and K

XI. Exchange reactions

Thermo: heat

Dynamics: movement

Thermodynamics is concerned with macroscopic properties (which are related to microscopic properties).

The entity under consideration is called the system. The rest of the universe is called the surroundings. A boundary separates the system from surroundings. The system can be open (if material can cross the boundary) or closed (if material cannot cross the boundary). The properties of a system are either intensive (independent of amount of matter) or extensive (dependent on amount of matter). When properties of a system change, it is said to undergo a change in state.

The chemical composition of a system is defined by phases and components. A phase is a macroscopically homogeneous, (in principle) physically separable portion of a system. The components of a system are the chemical constituents that are needed to describe the chemical composition of the system. The number of components is the minimum number required to describe the system.

A system is at equilibrium if it will not spontaneously change any of its properties even if an infinite amount of time is allowed to pass. The phases present when a system is at equilibrium are called stable phases (as opposed

to meta-stable phases). Meta-stable phases will react to form stable phases if *sufficient* time is allowed to pass.

The phase rule relates the number of components to the number of phases under equilibrium conditions: $p+f = c+2$, where p =# of phases, f =# of degrees of freedom, and c =# of components. The number of degrees of freedom are the number of independent variables that must be specified in order to fully define the system.

Heat (q) is a quantity that flows down a temperature gradient. A good illustration of heat flow is a system with two blocks of material initially at two different temperatures, T_1 and T_2 . No heat is allowed to cross the boundary of the system (it is perfectly insulated). What is observed is the lower T material increases in T , and the higher T material decreases in T until both materials have the same temperature, T_f . Sets of these experiments with different pairs of materials and different starting temperatures bear out the following general relationship (as long as no phase changes take place).

$$|q| \approx (m_1)(C_{p1}) |T_f - T_1| \approx (m_2)(C_{p2}) |T_f - T_2|$$

If heat flows into a system, q is positive; if it flows out, q is negative.

Work (w) is mechanical work *performed by* the system. The units of work are force times distance. A good way to think of work in the context of thermodynamics is as the product of pressure and change in volume.

The internal energy of a system (E) is made up of energies such as the potential energy from chemical bonds, the kinetic energy of the atoms and molecules in the system and the same for nuclear bonds. It is a quantity that we cannot determine in an absolute sense. We can, however, determine changes in E .

The 1st Law of Thermodynamics states that energy is conserved: $\Delta E = q - w$. The change in internal energy of a system is equal to the heat transferred to the system minus the work done by the system.